

Bloch electrons in a Jahn-Teller crystal and an orbital-density-wave state due to the Berry phase

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The effect of the Berry phase is included explicitly in the wavefunction describing conduction electrons in a crystal composed of periodically arrayed Jahn-Teller centers that have conically intersecting potential energy surfaces. The Berry phase can make a drastic change in the band structure, leading generally to the formation of an orbital-density-wave state. We discuss implications of our theory and possible relations to the orbital ordering observed in the manganese perovskites.

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The interplay among charge, spin, and orbital degrees of freedom is a central issue in recent study on the perovskite manganites such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [1]. In particular, the direct observation of the orbital ordering [2] makes the importance of the orbital degrees of freedom even clearer.

In this work, we investigate Bloch electrons in a Jahn-Teller (JT) crystal by focusing on the effects of double degeneracy of e_g orbitals at each MnO_6 octahedron, and its lift due to the Jahn-Teller (JT) distortions. Two groups have already reported the effects of the JT distortions on the electronic properties by implementing first-principles band-structure calculations [3,4]. Although these calculations are the state of the art, both groups overlook a very important ingredient of the problem, namely, the Berry phase or the geometric phase [5] associated with lattice distortions in each JT center in a crystal.

In view of this situation, we have done the following: First, by starting with a rather general argument on a periodic array of JT centers, we specify a simple model representing a linear chain of MnO_6 octahedra. On the basis of this model, we describe how the Bloch's theorem is modified in the presence of the Berry phase. Second, we show that its presence brings about a drastic change in the band structure compared to the result in its absence. This calls for revision of conventional band-structure calculations for materials involving the JT centers. Third, we find that the optimum JT distortions can be obtained by making the total energy minimum and that the resultant ground state exhibits an oscillation of the orbital density, the orbital density wave (ODW). In particular, the ODW is reduced to the orbital-ordering state with an appropriate choice of parameters involved in the system. Fourth, we envisage that many experimental results for the perovskite manganites related to the orbital degrees of freedom may be explained in the light of our theory.

Consider a periodic array of JT centers. Here the word “JT center” is used in a slightly broader sense than usual.

We use it for a complex of atoms whose vibronic states arise from the interaction of degenerate electronic states and linearly-coupled vibrational modes. (Note that the degeneracy does not necessarily come from the point-group symmetry.) Such a complex has structural instability which causes distortions of the atomic configuration, leading to the lift in the degeneracy of the electronic states at equilibrium. If more than two linearly-coupled vibrational modes are present, potential energy surfaces exhibit so-called “a conical intersection (CI)” [6]. The CI has also drawn much attention recently, due to the topological phase arising from it. This is an example of the Berry phase, which has been known in the context of dynamical JT effects for years [7].

We specify the JT center we consider in this paper. It is composed of two reference electronic states, ψ_a and ψ_b , and two vibrational modes, Q_a and Q_b , that couple with the electronic states linearly. In matrix representation using $\{\psi_a, \psi_b\}$ as a basis, the vibronic interaction is given by

$$\begin{pmatrix} \alpha Q_a & \beta Q_b \\ \beta Q_b & \gamma Q_a \end{pmatrix}. \quad (1)$$

This matrix is diagonalized to yield eigenvalues, $E^\pm = \{(\alpha + \gamma)Q_a \pm [(\alpha - \gamma)^2 Q_a^2 + 4\beta^2 Q_b^2]^{1/2}\}/2$, which possess a conically intersecting degeneracy point at $Q_a = Q_b = 0$, if $\alpha \neq \gamma$.

The isolated JT center described above is modified in a crystal. However, the CI seen in E^\pm survives against a perturbation preserving the time-reversal invariance [8]: Application of such a perturbation modifies the vibronic coupling matrix into

$$\begin{pmatrix} \alpha Q_a + a & \beta Q_b + b \\ \beta Q_b + b & \gamma Q_a + c \end{pmatrix}, \quad (2)$$

where real numbers a , b , and c represent perturbations from crystal environments, but this merely shifts the CI position to $Q_a = (c - a)/(\alpha - \gamma)$, $Q_b = -b/\beta$ [9].

Now we construct a model Hamiltonian H for the crystal composed of the JT centers. Using the vibronic interaction expressed in Eq. (1), H is given by

$$H = - \sum_{\langle i,j \rangle} (t_1 a_i^\dagger a_j + t_2 b_i^\dagger b_j + t_3 a_i^\dagger b_j + t_3 b_i^\dagger a_j + \text{h.c.}) \\ + \sum_j [(\alpha Q_{aj} + a) a_j^\dagger a_j + (\gamma Q_{aj} + c) b_j^\dagger b_j \\ + (\beta Q_{bj} + b) (a_j^\dagger b_j + b_j^\dagger a_j)], \quad (3)$$

where the first sum describes the electron transfer effects between the JT centers and $\langle i, j \rangle$ indicates a nearest-neighbor pair. The second sum is the electronic Hamiltonian part for the JT center at site j , where Q_{aj} and Q_{bj} are Q_a and Q_b at site j , respectively, and a_j and b_j are, respectively, annihilation operators for electrons in the states ψ_a and ψ_b . In the later discussion on manganese oxides, a_j and b_j are, respectively, identified as the electronic states stemming from $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals of Mn^{3+} , which are hybridized with oxygen orbitals.

In Eq. (3), the spin degree of freedom is neglected for simplicity, but this is legitimate for the perovskite manganites due to the Hund's coupling to the electrons in the t_{2g} orbitals. As for lattice vibrations, we have not included the unperturbed phonon Hamiltonian H_{ph} which treats the restoring forces for Q_{aj} and Q_{bj} as well as the kinetic-energy parts. In this paper, we restrict ourselves to the situation in which the electron density per site is constant at all JT centers. Then H_{ph} is reduced to a constant and thus it can be neglected.

Let us transform the electronic basis from $\{a_j, b_j\}$ into $\{c_j, d_j\}$, where $c_j \equiv (a_j + ib_j)/\sqrt{2}$ and $d_j \equiv (a_j - ib_j)/\sqrt{2}$. In this new basis, H is rewritten as

$$H = - \sum_{\langle i,j \rangle} (tc_i^\dagger c_j + td_i^\dagger d_j + sc_i^\dagger d_j + s^* d_i^\dagger c_j + \text{h.c.}) \\ + \sum_j [U_j (c_j^\dagger c_j + d_j^\dagger d_j) + V_j c_j^\dagger d_j + V_j^* d_j^\dagger c_j], \quad (4)$$

where $t = (t_1 + t_2)/2$, $s = (t_1 - t_2)/2 + it_3$, $U_j = [(\alpha + \gamma)Q_{aj} + a + c]/2$, and $V_j = [(\alpha - \gamma)Q_{aj} + a - c]/2 - i(\beta Q_{bj} + b)$. Note that the circular motion of Q_{aj} and Q_{bj} around the CI point $(Q_{aj}, Q_{bj}) = ((c-a)/(\alpha-\gamma), -b/\beta)$ changes the phase of V_j . This phase change is what responsible for the appearance of the Berry phase. Because we assume that the electron density per site is constant at all JT centers, the absolute value of V_j is independent of j , though its phase can vary from site to site.

For the e_g electrons in the MnO_6 octahedron, the sum of α and γ vanishes by symmetry. This makes the parameters U_j constant and these parameters can be removed by shifting the origin of energies. For this reason, we will not be concerned with the U_j terms.

We discuss the modification of the Bloch's theorem based on the model in Eq. (4) in one spatial dimension

with $t_1 = t_2$ and $t_3 = 0$ for the time being. This simplification leads us to an analytic expression without loss of essential physics. In this choice of parameters, H in momentum representation is reduced to

$$H = \sum_k \varepsilon_k (c_k^\dagger c_k + d_k^\dagger d_k) \\ + \sum_{k,q} (V_q c_{k+q}^\dagger d_k + V_q^* d_k^\dagger c_{k+q}), \quad (5)$$

where $\varepsilon_k = -2t \cos k$ and $V_q = (|V|/N) \sum_j e^{-i(qj - \xi_j)}$. Here we set the lattice constant as unity and N is the total number of sites.

Although it appears in V_q , the phase ξ_j does not play a role, if it is independent of site, i.e., $\xi_j = \xi$. In fact, the one-electron eigen energy for H is given by $E_k^\pm = \varepsilon_k \pm |V|$ in this case and the corresponding eigenfunction $\varphi_k^\pm(x)$ obeys the Bloch's theorem, characterized by the property

$$T \varphi_k^\pm(x) = \varphi_k^\pm(x+1) = e^{ik} \varphi_k^\pm(x), \quad (6)$$

with T the operator to translate the whole system by a unit lattice vector.

Imagine now that ξ_j changes from 0 to 2π site by site in the period of M JT centers. For simplicity, we assume that $\xi_j = 2\pi j/M$ and that M is commensurate with N . In this situation, V_q is given by $V_q = |V| \delta_{q, 2\pi/M}$ and the one-electron eigen energy is determined as

$$E_k^\pm = [\varepsilon_k + \tilde{\varepsilon}_k \pm \sqrt{(\varepsilon_k - \tilde{\varepsilon}_k)^2 + 4|V|^2}]/2, \quad (7)$$

with $\tilde{\varepsilon}_k = \varepsilon_{k+2\pi/M}$. The corresponding eigenfunction $\varphi_k^\pm(x)$ satisfies the modified Bloch's theorem:

$$T \begin{bmatrix} \varphi_k^+(x) \\ \varphi_k^-(x) \end{bmatrix} = e^{i(k+\pi/M)} U P U^{-1} \begin{bmatrix} \varphi_k^+(x) \\ \varphi_k^-(x) \end{bmatrix}, \quad (8)$$

where the matrices P and U are defined as

$$P = \begin{pmatrix} e^{i\pi/M} & 0 \\ 0 & e^{-i\pi/M} \end{pmatrix}, \quad U = \begin{pmatrix} p_k^+ & p_k^- \\ -p_k^- & p_k^+ \end{pmatrix}, \quad (9)$$

with p_k^\pm , given by

$$p_k^\pm = \left[\frac{1}{2} \pm \frac{\tilde{\varepsilon}_k - \varepsilon_k}{2\sqrt{(\tilde{\varepsilon}_k - \varepsilon_k)^2 + 4|V|^2}} \right]^{1/2}. \quad (10)$$

In addition to the ordinary phase factor e^{ik} , the Bloch function acquires the Berry phase. It takes account of the difference in the electron motion around the JT center, clockwise or counterclockwise, indicating that careful treatments are needed for the analysis of a system including JT centers.

The phase factor $e^{i\pi/M}$ in Eq. (8) assures single-valuedness of basis functions which satisfy $T^M \varphi_k^\pm(x) = e^{iMk} \varphi_k^\pm(x)$ in accordance with the Bloch's theorem in a crystal with the lattice constant M ; without it, signs of

basis functions change after the translation by an odd M number of sites. This factor may be considered as one arising from “a fictitious magnetic field” that exists at each CI [10]. On the other hand, P accounts for the site-to-site variation of the lattice-twisting phase ξ_j .

The dispersion curves representing E_k^\pm are plotted in an extended Brillouin zone for various values of M in Fig. 1 in which $|V|/t$ is taken to be 0.5 and the origin of momenta is shifted by $-\pi/M$ in each panel. This shift is equivalent to use $K = k + \pi/M$ instead of k , where K is the generalized quasi-momentum and π/M arises from the fictitious magnetic field [11].

For $M = \infty$ (or $M = 1$), the dispersion relation $E_k^\pm = \varepsilon_k \pm |V|$ is the one corresponding to the result in the conventional band-structure calculation [3,4]. For $M = 2$, we observe the same band gap with the magnitude of $2|V|$ as that for $M = \infty$, but the dispersion curve itself is completely different. We can even predict an insulating state at “half-filling”, where the electron density per site n is unity. For the case of $2 < M < \infty$, we also find a drastic change in E_k^\pm from that for $M = \infty$, but the system remains metallic irrespective of n .

For given n , M and $|V|/t$, information on the dispersion relation allows us to evaluate the ground-state energy $E_M(V)$ by filling electrons in the one-electron states from the bottom. The relative stability among the states with different M 's can be determined by comparing these $E_M(V)$'s. A typical result is shown for $|V|/t = 0.5$ in Fig. 2 in which $\delta E(V, M)$, defined by $\delta E(V, M) \equiv E_M(V) - E(V = 0)$, are given as a function of n . Note that at $V = 0$, the ground-state energy is independent of M . Thus $E(V = 0)$ is written without the suffix M .

The result in Fig. 2 indicates that each M has a characteristic electron filling, $n(M)$, at which $\delta E(V, M)$ takes a local minimum. For an arbitrary V , $n(M)$ can be evaluated only numerically, but for $|V|/t \ll 1$ and small M , it turns out that $n(M)$ is well approximated by $n(M) = 2/M$ (and $n(M) = 2 - 2/M$ due to the particle-hole symmetry). The comparison of $\delta E(V, M)$'s suggests that the JT-distorted state with the period M is expected to occur spontaneously for n around $n(M)$. Note that $\partial E/\partial n$ exhibits a jump at $n = n(M)$ only for $M = 2$ due to the insulating nature. For other M 's, no jump can be seen at $n = n(M)$.

From the viewpoint of our theory, we now try to understand the orbital ordering observed in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. We concentrate our interest into the case of $x = 0$ or LaMnO_3 which corresponds to the half-filling in our model. At $n = 1$, the above discussion on the ground-state energy implies that a periodic JT-distorted state with $M = 2$, or an ODW state composed of bipartite A and B sublattices, is stabilized. This agrees qualitatively well with the experimental situation.

As for the orbital pattern, LaMnO_3 exhibits an orbital order between the orbitals of $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ rather

than $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. In order to see whether this pattern can be predicted in our theory or not, we take a more realistic choice of parameters. For this purpose, we set the hopping energies as $t_1 = 3t_0/4$, $t_2 = t_0/4$, and $t_3 = \sqrt{3}t_0/4$ by assuming that both ψ_a and ψ_b are purely d -wave-like. Here the energy unit t_0 is the overlap integral between adjacent $d_{3z^2-r^2}$ orbitals situated in the z -direction. In this choice, t and s are, respectively, given by $t = t_0/2$ and $s = (t_0/2)\exp(i\pi/3)$. On the other hand, we set $|V|$ as t_0 by referring to the result of band-structure calculations [3] in which the band gap due to the JT distortions, $2|V|$, is seen to be about the same as the bandwidth of the e_g electrons.

With these parameters, we can determine ξ_j at A and B sublattices, ξ_A and ξ_B , by optimizing the ground-state energy, leading to $\xi_A = \pi/3$ and $\xi_B = 4\pi/3$ (or $\xi_A = 4\pi/3$ and $\xi_B = \pi/3$). The phase difference, $|\xi_A - \xi_B| = \pi$ reflects the Berry-phase effect which is fixed by the condition $M = 2$, while the phase $\pi/3$ takes account of the local phase due to the complex number s .

In order to see the orbital ordering in real space described by the ground state obtained in this way, we evaluate the following quantities:

$$\rho_{3x^2-r^2}(j) = \langle \phi_{xj}^\dagger \phi_{xj} \rangle, \quad \rho_{3y^2-r^2}(j) = \langle \phi_{yj}^\dagger \phi_{yj} \rangle, \quad (11)$$

where ϕ_{xj} and ϕ_{yj} are, respectively, the annihilation operators for electrons in $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals at site j . These operators are given by the linear combination of a_j and b_j through $\phi_{xj} = \cos(2\pi/3)a_j + \sin(2\pi/3)b_j$ and $\phi_{yj} = \cos(4\pi/3)a_j + \sin(4\pi/3)b_j$.

In Fig. 3, the calculated results for $\rho_{3x^2-r^2}$ and $\rho_{3y^2-r^2}$ are shown as a function of the site index j . The alternating pattern between $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals emerges. Thus we may call the present ODW state as “the orbital-ordering state”. Note that “the orbital-ordering state” is obtained without making any fine tuning of parameters. In fact, the obtained ODW state is not easily destroyed by changing the hopping parameters around the present values. However, it is destroyed completely, if we do not pay due attention to the Berry phase, as shown in the lower panel in which we take $\xi_A = \xi_B = 0$.

We have also obtained following speculations: First, the interband transitions between E_k^- and E_k^+ are radically different from $M = \infty$ to $M = 2$. In the former, no spectral band is expected but it is expected in the latter. This may be connected with the observed anomalous optical spectra [12]. Second, because the Berry phase represents a fictitious magnetic field, application of “real” magnetic fields provides a profound effect on the ODW. This may be the key to explain the observed successive phase transitions in magnetic fields [13]. These facts among others may support a Berry-phase scenario to understand the orbital ordering in the manganese perovskites, although we need to make our model more realistic to compare with the real situations.

In conclusion, we have demonstrated the importance of the Berry phase in the calculation of band structures for crystals containing JT centers.

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- [1] See, for example, P. G. Radaelli *et al.*, Phys. Rev. B **55**, 3015 (1997) and the references therein.
 - [2] Y. Murakami *et al.*, to appear in Phys. Rev. Lett.
 - [3] W. E. Pickett and D. J. Singh, Phys. Rev. B **53**, 1146 (1996).
 - [4] I. Solov'yev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).
 - [5] M. V. Berry, Proc. Roy. Soc. A **392**, 45 (1984).
 - [6] See, for example, D.R.Yarkony, Rev. Mod. Phys. **68**, 985 (1996) and the references therein.
 - [7] H. C. Longuet-Higgins *et al.*, Proc. Roy. Soc. London, Ser.A **244**, 45 (1958); G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963).
 - [8] H. C. Longuet-Higgins, Proc. Roy. Soc. London A **344**, 147 (1975).

- [9] If the perturbation breaks the time-reversal invariance, the off-diagonal elements usually acquire imaginary parts, resulting in the disappearance of the CI.
- [10] C. A. Mead, Chem. Phys. **49**, 23 (1980).
- [11] See, for example, E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics Part 2*, Section 56, (Pergamon Press, London 1980).
- [12] Y. Okimoto *et al.*, Phys. Rev. Lett. **75**, 109 (1995).
- [13] H. Kawano *et al.*, Phys. Rev. B **53**, R14709 (1996).

FIG. 1. Dispersion curves for several values of M with $|V|/t = 0.5$. We shift the origin of momenta by $-\pi/M$ in each panel.

FIG. 2. Stabilization energy of the M -period JT distorted state as a function of the electron filling n for $|V|/t = 0.5$. We note that $\delta E_M(V)$ is in proportion to $|V|^2$ for $|V|/t \ll 1$ and the proportional coefficient depends on M .

FIG. 3. Orbital densities, $\rho_{3x^2-r^2}$ and $\rho_{3y^2-r^2}$, as a function of site j for $t = t_0/2$ and $s = (t_0/2)\exp(i\pi/3)$. In the upper panel, ξ_A and ξ_B are determined by optimizing the ground-state energy, while in the lower panel, we set $\xi_A = \xi_B = 0$.

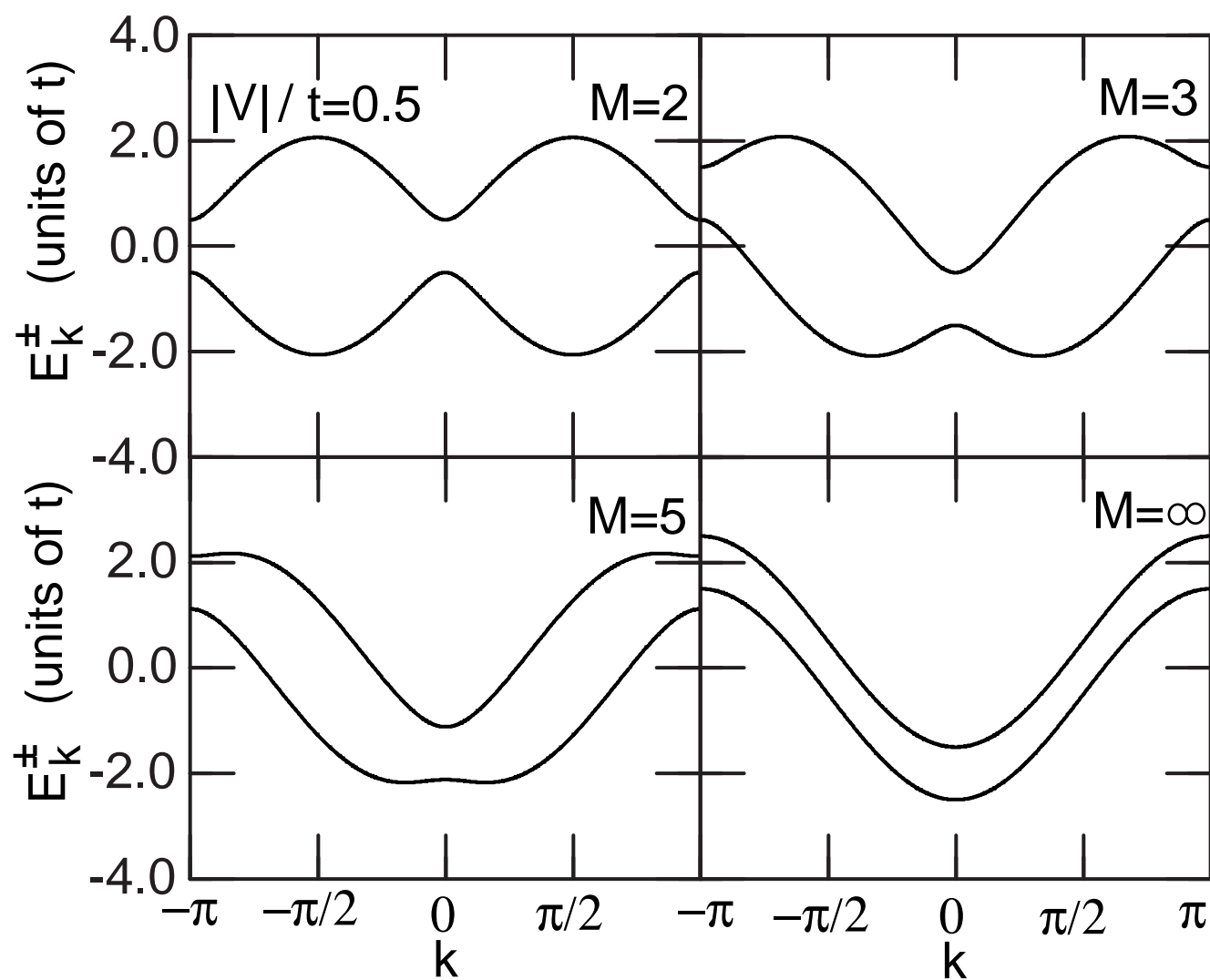


Fig.1 Koizumi et al.

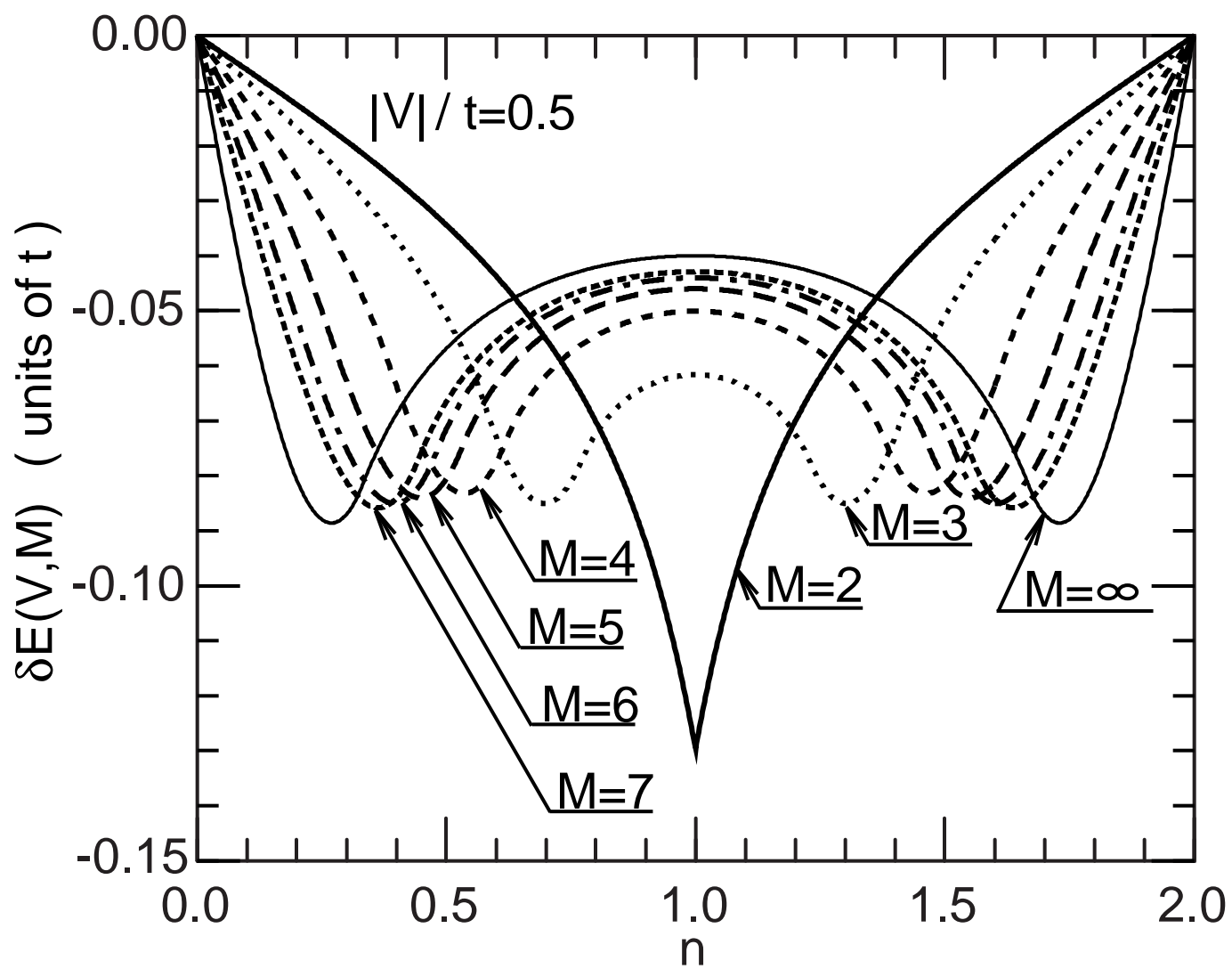


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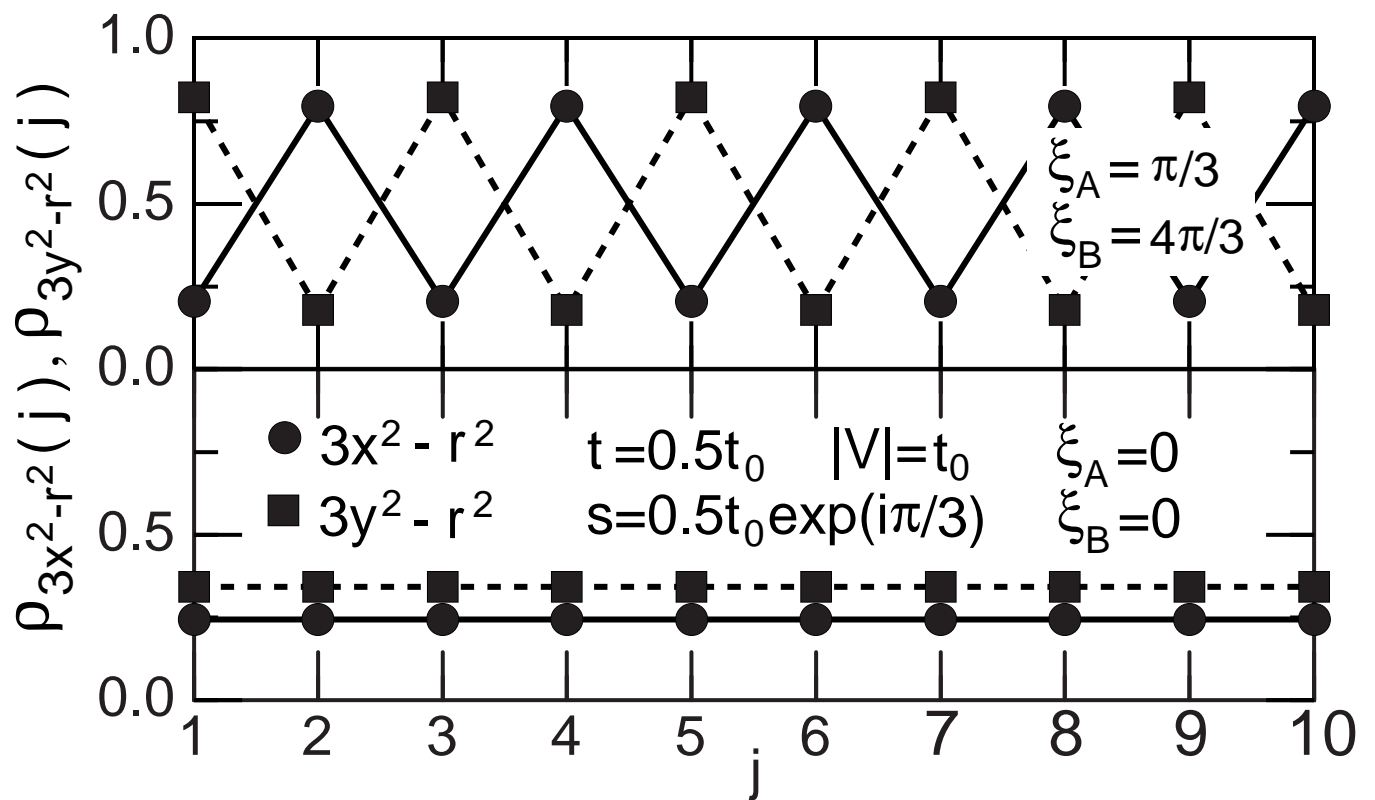


Fig.3 Koizumi et al.